

THE ANALYST.

NOVEMBER, 1892.

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

THE first Meeting of the Session was held at the Rooms of the Society of Arts, John Street, Adelphi, on Wednesday, 5th October. The chair was occupied by the President (Mr. O. Hehner).

The minutes of the last meeting were read and confirmed.

The following gentlemen were duly elected Members of the Society:—Messrs. Gustavo Antonio Abrines, E. J. Bevan, and John Bate Nickolls.

Dr. Sykes temporarily occupied the chair during the reading and discussion of the following paper:—

ON THE INFLUENCE OF ALUMED BAKING POWDER ON PEPTIC DIGESTION, WITH REMARKS ON A RECENT PROSECUTION.

BY OTTO HEHNER.

It is well known to public analysts that in 1880 the Recorder of Cambridge decided that baking powder could not be considered an article of food, and did not, therefore, come within the scope of the Sale of Food and Drugs Act, and that, even if it did, the presence of alum in baking powder did not render it injurious to health. In consequence of this decision, alumed baking powder has ever since been freely and extensively sold throughout the country.

All public analysts being agreed to regard alum in bread as an adulteration, and alumed bread having, in consequence, practically disappeared, the decision of the above-mentioned Recorder has always appeared to me, as no doubt to most of my colleagues, to be both illogical and absurd, as well as detrimental to the interests of the consumers. Knowing that in the Midlands especially the sale of alumed baking powder was very common, I brought the matter before one of the County Councils for which I act as public analyst, and received their sanction to bring a case into Court, in the hope of obtaining a reversal of the Cambridge decision.

Among several samples of baking powder submitted to me for analysis was one which gave the following analytical results :—

Alumina	...	...	...	4.97	per cent.
Carbonic acid	...	...	...	9.76 & 9.85	„
Sulphuric acid	...	...	...	15.13	„
Ammonia	...	...	...	0.12	„
Starch	...	...	...	33.40	„
Residue on ignition	...	...	...	31.11	„

From these figures the composition of the baking powder was calculated to be as follows:—4.97 per cent. of alumina correspond to 45.80 per cent. of crystallised potash alum, while 15.13 per cent. of sulphuric acid equals 44.58 per cent. alum. The carbonic acid corresponds to 18.63 and 18.80 per cent. of sodium bicarbonate. Subtracting from the ash the anhydrous alum calculated from the amount of crystallised alum (24.96), there is left 6.15 per cent. of soda, equal to 16.66 per cent. of bicarbonate, a figure approximating sufficiently near to the amount calculated from the carbonic acid determination. Thus the entire composition of the powder was :—

Crystallised alum	...	...	...	...	45.80
Bicarbonate of soda	...	...	...	...	18.71
Starch	...	...	...	...	33.40
Moisture and not determined	...	...	...	...	2.08
					100.00

Nearly one-half of the sample consisted, therefore, of alum, while the article upon which the prosecution in 1880 was based contained but 29 per cent. of crystallised alum.

On Feb. 18th, 1880 (ANALYST, vol. v., p. 67), Mr. West Knights brought a number of experiments before this society, which showed in a marked manner the profound influence of alum in artificial digestions of bread and flour, but inasmuch as I expected that it would be argued, as indeed it was at the hearing of the case, that alum was quite a different thing to alumed baking powder, and that in the latter the alumina was rendered insoluble by precipitation with sodium bicarbonate, I undertook a number of experiments with alum, as well as with alumed baking powder, to test this matter, and the results of this research I propose now to lay before you.

Theoretically, one equivalent of alum should require for complete precipitation six equivalents of sodium bicarbonate, or 948 parts of alum, 504 parts of sodium bicarbonate. The 18.71 parts of sodium bicarbonate contained in the sample should be able to precipitate 35.19 parts of alum, while 45.80 were actually present. It should be expected, therefore, that when the baking powder in question had been mixed with water, after the completion of the reaction a considerable amount of alumina would be left in solution as

alum. I found, however, while there certainly was a marked trace of alumina left in solution, its quantity was less than is required by theory. No doubt the reaction is somewhat more complicated than might at first be expected, not only pure hydrated alumina but also basic alumina salts being precipitated, thus giving the bicarbonate a somewhat greater precipitating power than would correspond to the above proportions. In any case, we have to deal with precipitated alumina hydrate, with basic sulphate of alumina, and with some soluble salt of the base.

According to the directions on the wrapper furnished me, in which the sample had been sold, a heaped teaspoonful of the powder was recommended to be used to every pound of flour. I found the weight of an ordinary teaspoonful to be, on an average of six weighings, 11.21 grammes. Assuming that two pounds of flour furnish three pounds of bread, a four-pound loaf of bread made in the manner directed on the wrapper would contain no less than 210 grains of alum.

Experiments on the Digestion of Egg-albumen.

A solution of pepsin was made, containing 0.02 gramme of pepsin in 100 c.c. of water. It had previously been ascertained that the pepsine in question was very active and was capable of digesting, under favourable conditions, 2,500 times its weight of hard-boiled white of egg, at 50° C., in about three to four hours. 5 c.c. of the pepsin solution contained, therefore, one milligramme of pepsin and was able to dissolve 2.5 grammes of white of egg in a fluid containing 0.2 per cent. of hydrochloric acid. In a few preliminary blank experiments this was found to be the case, while in the presence of baking powder, in proportion equal to that recommended by the manufacturer, a considerable quantity of albumen could not be brought into solution; a similar residue was observed when alum itself, to the extent of one-half of the quantity of baking-powder, was added in another trial. Quantitative experiments were then made.

Experiment 1.—Two grammes of hard-boiled white of egg and 0.05 gramme of baking powder were digested with one milligramme of pepsin for five hours. The residue left was washed with a little cold water, and the insoluble nitrogen determined by Kjeldahl's process. 0.0407 gramme of dry albumen, corresponding to 0.28 of fresh white of egg (with 85.5 per cent of moisture), or 14 per cent. of the amount taken, was found insoluble.

Experiment 2.—A precisely similar experiment was made, only instead of baking powder the corresponding amount of crystallised alum (0.025 gramme) was taken. Left insoluble 0.0402 dry albumen, or 13.8 per cent. of the amount taken.

Experiments 3 and 4.—In two other similar experiments with the same proportion of baking powder and alum as before, 0.0812 and 0.0743 dry albumen were left, corresponding to 28.0 and 25.6 per cent. of the wet albumen taken.

Experiments 5 and 6.—In these the quantity of baking powder and alum taken was increased four-fold, namely, to 0.2 and 0.1 gramme for 2 grammes of white of egg respectively. There were left, after six hours' digestion, 46.7 and 39.2 per cent. of the albumen taken.

Experiment 7.—This was a repeat experiment, with 0.1 gramme of alum for 2 grammes of white of egg. After 6 hours there were left 52.7 per cent of undigested white of egg.

It is seen that on repetition closely corresponding results could not be obtained, for although the egg had been rubbed through a very fine wire sieve, it was apt to cake together with the formation of little lumps, which could not be easily separated by shaking. But, speaking generally, the results show that the same quantities of alum, either taken pure or in the form of baking powder, prevent to an equal extent the digestion of hard-boiled white of egg. Parallel with every set of trials a blank experiment was made, without alum or baking powder, and the white of egg was in every case completely dissolved. As far as egg-digestion, therefore, is concerned, alumed baking powder is quite as injurious as alum itself.

Experiments on the Digestion of Wheat Flour.

Wheat-flour, containing 1.73 per cent. of nitrogen, corresponding to 10.81 per cent. of albuminoids, was similarly digested. In a blank experiment, without alum or baking powder, there was left undissolved after six hours' digestion of two grammes, 0.0280 gramme of albumen, or 12.9 per cent. of the albuminoids.

Experiment 8.—In the presence of 0.05 gramme of baking powder, with (nearly) 0.025 gramme of alum, there was left undissolved after six hours 0.0318 gramme, or 14.9 per cent.

Experiment 9.—When the amount of baking powder added was fourfold, namely 0.2 gramme, the same percentage of albuminoids was left undissolved, 0.0318 gramme, or 14.9 per cent. remaining.

Experiment 10.—With an amount of alum corresponding to 0.05 gramme of baking powder, viz., 0.025 gramme alum, there remained after six hours a residue of albuminoid of 0.0743 gramme, or 34.4 per cent. of the total amount taken.

Experiment 11.—With the fourfold amount of alum there remained 0.1187 gramme, or 54.9 per cent.

In the case of digestion of flour, therefore, alumed baking powder has far less influence than the corresponding amount of alum contained in it. Alum itself has a most injurious influence upon the digestion of flour, while that of alumed baking powder is slight.

Experiments with Bread.

Experiment 12.—Two grammes of the crumb of bread free from alum were digested as before. The residue left after six hours was Kjeldahled and found to contain nitrogen corresponding to 0.0231 gramme albuminoids. Unfortunately, the percentage of nitrogen in the bread itself was not determined; hence the results in the following experiments can only be judged by comparison, but no great error can be committed if it be assumed that the bread contained 7 per cent. of albuminoids, which is the mean given by Koenig in his vast collection of analytical results. In this case 16.5 per cent. of the total were left undissolved.

Experiment 13.—Two grammes of the bread-crumbs, digested with 0.05 gramme baking powder, left 0.0315 gramme albuminoids undigested; or, calling the amount left in the blank 100, there were left 136.3, or 22.5 per cent. of the amount taken.

Experiment 14.—With 0.2 gramme of baking powder there remained undissolved 0.0407 gramme albuminoids, or 172.6 per cent. in comparison with the blank, or 29.1 per cent. of the original amount taken.

Experiments 15 and 16.—In corresponding experiments with alum only, namely, 0.025 and 0.1 gramme, there were left 0.0315 and 0.0516 gramme. These figures correspond respectively to 136.3 and 223.4, compared with the blank, or to 22.5 and 36.9 per cent. of the total albumen taken.

Curiously, therefore, the influence of baking powder containing alum upon the digestion of bread is more marked than in the case of the raw flour. With small amounts, or rather the amount of baking powder recommended to be taken by the manufacturer, the influence of alum and of alumed baking powder is equal, but with larger quantities the alum acts more detrimentally than does the baking powder.

Experiments with Milk.

Experiment 15.—5 c.c. of milk were digested for six hours without the addition of either alum or baking powder. There were left insoluble 0.0465 gramme of albuminoids. In this case also the total amount of albuminoid in the milk had not been estimated, but taking 3.66 to be the average of albuminoids in genuine milk, there was left 63.5 per cent. of the total nitrogenous matter taken.

Experiment 16.—5 c.c. of the same milk, digested with 0.05 gramme of baking powder, left 0.0681 grammes of albuminoids, or, calling the amount left in the blank experiment 100, there remained 146.5, or 93 per cent. of the amount of albuminoids taken.

Experiment 17.—Adding the fourfold quantity of alumed baking powder, there were obtained exactly similar figures, namely, 0.0681 gramme, or 146.5 compared with the blank, or 93.0 per cent. of the total taken.

Experiments 18 and 19.—Using the corresponding amount of crystallised alum, namely, 0.025 and 0.1 gramme, there were left in each case 0.0562 gramme of nitrogenous matter undigested, or, compared with the blank as 100 to 121 parts, or 76.7 per cent. of the amount taken.

It is remarkable that in the digestion of milk the alumed baking powder exerts a more injurious influence than does the amount of alum contained in it, and the smaller amount of alum, whether taken as baking powder or as crystallised alum, acts as markedly as does the four times larger quantity.

Experiments 20, 21, and 22.—In order to ascertain whether baking powder free from alum had any retarding influence upon digestion, three trials were made :—A blank digestion of hard-boiled white of egg, without baking powder ; a similar experiment with the addition of 0.05 gramme of alum-free baking powder, and a third with 0.2 gramme of the same baking powder. In all three cases the whole of the white of egg dissolved in five hours, nothing insoluble being left.

It is evident that in the digestion of egg, at least, alum-free baking powder is without detrimental influence.

Physiological Experiments.

I weighed out four quantities of alumed baking powder, amounting to two grammes. This is very nearly the quantity which would be contained in four ounces of bread, if made according to the directions on the label (the exact amount would be 1.88 grammes), mixed them with water, waiting until the effervescence had finished, added some sugar to render the dose palatable, and took one dose myself, giving the other three to my assistants. I requested them to let me know next morning their symptoms, without previous communication with each other. We were all in perfect health before taking the dose. Already, about an hour-and-a-half afterwards, unpleasant symptoms began to appear. Speaking for myself, I experienced first a feeling of great weight in the region of the stomach, later on pains in the epigastric region, slight difficulty in breathing, headache, and ultimately slight diarrhoea,—symptoms resembling an attack of indigestion. My assistants were similarly affected, and felt discomfort for several days.

After complete recovery, I took in a similar manner one gramme of the powder, or a quantity which would be contained in as little as two ounces of bread. Similar symptoms, almost to an equal degree, manifested themselves.

I have, therefore, come to the following conclusion :—that alumed baking powder exerts a most injurious influence upon digestion, whether artificial or within the body ; that the presence of alum in baking powder must be regarded as an adulteration injurious to health ; that samples containing alum should be condemned as injurious, even though magistrates and recorders declare alum to be quite harmless ; and that the sodium

bicarbonate contained in the baking powder does not neutralise the objectionable qualities of the alum. This, indeed, was not to be expected upon chemical grounds, inasmuch as the precipitated hydrate of alumina is readily soluble in dilute acid, and in the baking of bread the temperature does not rise in the interior of the loaf to anything like the point at which hydrate of alumina loses its water of constitution.

At the hearing of the case in question certain evidence was given for the defence, to which I will shortly refer. Mr. Wynter Blyth, who in his work on "Foods" declared "there can be no difference of opinion that it (alum in bread) is a serious adulteration, and not to be permitted," and who has, in his capacity as public analyst, condemned samples of bread containing alum as adulterated, came forward on behalf of the manufacturers of this baking powder, and stated that he considered alum in bread to be an entirely different thing to alum in baking powder; and that he had for some time past used in his household bread made with the baking powder in question without experiencing any injurious effects. Mr. F. Sutton, public analyst, who, as far back as 1872, had given a testimonial to the identical maker of this baking powder, in which it was lauded in the strongest language, went further, and attributed to alumed baking powder the valuable property of fattening pigs, if added to their ordinary food. He would continue to condemn alum in bread, but would not object to alumed baking powder. Dr. Thudichum, who, not being a public analyst, felt himself still freer from restraint, strongly stated that he considered alum itself to be possessed of valuable digestive properties. No attempt was made on the part of these three gentlemen to rebut the digestion experiments which I laid before the Bench, as I now lay them before you to-night, only the general statement being made that natural gastric juice was an altogether different thing from the artificially prepared article; and that as to my personal feelings and those of my assistants, all that could be urged was that we must have persuaded ourselves we were ill when all the time in reality we were perfectly well.

The magistrates, in view of this conflict of evidence, which certainly was quite unreconcilable, dismissed the case upon the same grounds as those enunciated by the Recorder of Cambridge.

I trust that my present contribution to the subject will go some way towards advancing the matter to a final and more satisfactory settlement. It is clearly my opinion¹ that as public analysts we should be acting contrary to public interests if we passed alumed baking powder as a genuine and legitimate article.

My best thanks are due to my assistant, Mr. W. P. Skertchly, for carrying out the analytical work involved in this investigation.

DISCUSSION.

The Chairman, in inviting discussion, said he felt sure that the members present had all listened with much interest to the paper just read. Mr. Hehner had gone into

the experimental side of the question very fully, and he (the chairman) thought that the strong evidence as to the deleterious action of alumina on the human economy which had been brought before them that evening, could not fail to convince any unbiased mind that its presence in baking powder was highly undesirable.

Mr. Cassal thought it desirable that by some expression of opinion on the part of the members of the Society the president should be supported in his position in the baking powder case under notice, of which, of course, they had all heard. It was extremely unfortunate that prominent public analysts should appear in Court and should give evidence against one another—especially evidence of the kind they had heard about, and he was exceedingly surprised at the statements which Mr. Wynter Blyth and Dr. Thudichum made in the case. It was equally regrettable that Mr. Sutton, who was a well-known public analyst, should have given the evidence that he was reported to have given. He (Mr. Cassal) gathered from what the president had said that hydrate of alumina was to be regarded as, in a sense, equally injurious with alum, and as, in fact, *the* injurious substance which might be present in bread that had been made from alumed baking powder. The contention of Messrs. Blyth and Sutton appeared to be that alum, as alum, was the only thing that could be injurious in bread or flour. It was very important that the president's experiments should be made known, as far as possible, among public analysts, inasmuch as they appeared to show that hydrate of alumina was in itself a distinctly injurious substance. That at once disposed of the only argument that Messrs. Blyth and Sutton had, namely, that carbonate of soda having precipitated hydrate of alumina, alum could no longer be present as such, and, therefore, that there could be no injury to the health of the consumer. It must be plain to the society that if the magistrates had properly appreciated the weight of the evidence before them, they ought to have given their decision in favour of the County Council. It was plain enough that they had definite scientific experiments on the one side, and mere assertions, of little or no scientific value, on the other. He therefore felt that the meeting would be perfectly justified in supporting the president of the Society, and in expressing their regret that two prominent public analysts—and two prominent members of the Society—should have given the evidence that they had given on that occasion.

Mr. H. Droop Richmond said it appeared to him that the president's experiments were hardly as conclusive as might have been wished. For instance, the experiments which he had made, and in which he and his assistants had swallowed alumed baking powder, were not, to his mind, conclusive. When given in that form it was concentrated, but if the same quantity were put into bread, it was spread over a much larger surface, and consequently only a small quantity of the alum was exposed to the action of the pepsin in the stomach. He believed that if the experiments were repeated, and if the president and his three assistants ate four ounces of bread containing the baking powder, the experiments would be more conclusive. He thought that in the case of bread, the peptic

digestion only played a small part in the total digestion. Pepsin had no amylolytic function, and the starchy portion would protect the remainder from attack during the short time it remained in the stomach; he believed that the pancreatic digestion played the more important part. He hoped that if the president were going to make any more experiments, he would try them with pancreatic extract, and see if there was the same retarding effect there. He did not wish it to be inferred, in suggesting to the president that he should make other experiments, that the experiments already carried out were not worth anything, because he thought they were extremely valuable, but he did not think they had gone as far as they could have been pushed.

The President felt bound to say, in reply to Mr. Richmond's remarks, that he thought, given plenty of gastric or pancreatic juice, the food might have been digested in spite of the alum. Probably individuals in very good health, and blessed with excellent digestions, might be able to digest bread even if it contained alum. What he did wish to lay particular stress upon was, that an article which, when taken in a moderate quantity and diluted with water, was injurious, should not be used in food. Of course, the injurious effects might be minimised in the case of a healthy person.

Mr. Cassal asked whether the case was appealed against, or whether there was any question of appealing? He supposed the usual excuse was made that a decision had been given on a question of fact and not of law.

The President replied that the County Council came to the conclusion that it was no use appealing, since evidence similar to that given at Ilkeston would certainly be brought forward again; and in view of a direct conflict of evidence an appeal would probably fail.

Mr. Cassal pointed out that the decision of the Recorder of Cambridge, or the decision of a magistrate, did not make law, and had really no weight at all; and he would take the opportunity of suggesting that whenever possible these gentlemen should be set right as far as was practicable. He thought it a very excellent thing to do in the interests of the public. Moreover, the very unfortunate circumstances which the President deplored, were only brought out on occasions of that kind, and they could hardly hope for the reforms required, unless the evil was clearly before the members of the profession.

The President wished to add that the case referred to was not finally decided and could be taken up again at any time. He had brought these experiments forward in order gradually to accumulate matter for such a contingency.

The President then resumed the Chair, and Mr. Skertchly read the following paper:—

NOTES ON W. F. K. STOCK'S NITROGEN PROCESS.

BY W. PEARSON SKERTCHLY.

IN THE ANALYST, vol. xvii., No. 194, appeared a paper by Mr. W. F. K. Stock on a "New and Rapid Method for the Determination of Nitrogen in Organic Bodies." The process

is based upon the oxidation of the substance by a mixture of strong sulphuric acid and manganese dioxide. This paper was read before a meeting of the members of the Society in May last, and, from the discussion which followed the reading of the paper, it appears that several members cast considerable doubt on the accuracy of the method, fearing that the use of manganese dioxide would cause considerable error in the estimation of the nitrogen.

Mr. Stock wrote a supplementary paper (*THE ANALYST*, xvii., 196), to prove that there was not the slightest danger of losing any nitrogen if the process was properly carried out.

I have also made a series of experiments to test the efficacy of the method, both with pure ammonia salts and with various nitrogenous organic substances. The figures that I obtained in my analyses I now wish to bring before you.

A solution of crystallized ammonium sulphate was made up, and two separate distillations gave 0.15895 gram. and 0.15810 gram. as the ammonia (NH_3) contents of 20 c.c. of this solution.

20 c.c. of the solution were now evaporated to dryness, with the addition of a few drops of dilute sulphuric acid, and treated with 10 c.c. of strong sulphuric acid and 5 grms. of manganese dioxide, in the way described by Mr. Stock, heating the mixture for ten minutes on a sand-bath. On distillation I obtained 0.15970 gram. NH_3 or 100.7 per cent. of the quantity taken.

Another 20 c.c. of the solution were treated exactly the same as in the above experiment, except that the heating on the sand-bath was continued for three-quarters of an hour. I recovered 0.15844 gram. NH_3 or 99.95 per cent.

The same quantity of the solution was then evaporated, and to it was added 1 gram. of pure cane sugar. It was now heated with 15 c.c. of strong sulphuric acid and 7 grms. of manganese dioxide. A dark green colour appeared after heating for fifteen minutes. The ammonia was distilled off, and gave 0.15923 gram. NH_3 , or 100.4 per cent.

As the amount of ammonia taken was so small, I think that these results are quite passable.

A sample of Dog-biscuit was analysed by this method, and gave the following results:—

<i>Kjeldahl.</i>	<i>New Method.</i>
3.43 per cent. Nitrogen.	3.51 per cent. Nitrogen.
4.16 „ Ammonia.	4.26 „ Ammonia.

A sample of Cotton-meal gave good results:—

<i>Kjeldahl.</i>	<i>New Method.</i>
4.01 per cent. Nitrogen.	3.94 per cent. Nitrogen.
4.87 „ Ammonia.	4.78 „ Ammonia.

Wheat-flour is very easily analysed by this method, as it is in such a fine state of division. The results obtained were :—

<i>Kjeldahl.</i>		<i>New Method.</i>	
1.73 per cent.	Nitrogen.	1.72 per cent.	Nitrogen.
2.10	„ Ammonia.	2.09	„ Ammonia.

Coffee is rather difficult to analyse, owing to an excessive amount of frothing when heated even gently with sulphuric acid and manganese dioxide, and also because some of the pieces of coffee are carried up the sides of the beaker by the froth, and remain unacted upon. This latter difficulty, of course, may be got over by reducing the coffee to a very fine powder. I find that the frothing is to a great extent avoided by heating the 2 grm. of the sample with 20 c.c. of concentrated sulphuric acid alone, and then, when the coffee is completely dissolved, cautiously adding the manganese dioxide. The mixture now simply requires to be left on the sand-bath until a green colour distinctly appears.

A sample of Coffee gave the following results :—

<i>Kjeldahl.</i>		<i>New Method.</i>	
2.30 per cent.	Nitrogen.	2.23 per cent.	Nitrogen.
2.79	„ Ammonia.	2.70	„ Ammonia.

A sample of commercially pure Gelatin gave satisfactory results :—

<i>Kjeldahl.</i>		<i>New Method.</i>	
15.68 per cent.	Nitrogen.	15.57 per cent.	Nitrogen.
19.04	„ Ammonia.	18.90	„ Ammonia.

I now proceeded to analyse six samples, rich in nitrogen, kindly given to me by Dr. Bernard Dyer, and in which he had estimated the nitrogen by the Kjeldahl method.

The following is a list of the substances examined, and the percentages of nitrogen (and ammonia) found in each, by Dr. Dyer and myself :—

LINSEED CAKE—

<i>New Method.</i>		<i>Kjeldahl.</i>		<i>Dr. Dyer's figures (Kjeldahl.)</i>	
Nitrogen.	Ammonia.	Nitrogen.	Ammonia.	Nitrogen.	Ammonia.
3.49 p.c.	4.25 p.c.	3.87 p.c.	4.70 p.c.	3.91 p.c.	4.74 p.c.

CRUSHED HOOFS AND HORNS—

13.37 p.c.	16.23 p.c.	15.34 p.c.	18.62 p.c.	15.38 p.c.	18.68 p.c.
13.30 p.c.	16.15 p.c.				

FISH GUANO (1)—

7.80 p.c.	9.47 p.c.	9.27 p.c.	11.25 p.c.	9.24 p.c.	11.22 p.c.
7.72 p.c.	9.37 p.c.				

FISH GUANO (2)—

4.94 p.c.	6.00 p.c.	5.50 p.c.	6.68 p.c.	5.60 p.c.	6.80 p.c.
4.97 p.c.	6.03 p.c.				

DRIED BLOOD—

10.81 p.c.	13.12 p.c.	12.93 p.c.	15.65 p.c.	13.08 p.c.	15.88 p.c.
10.82 p.c.	13.14 p.c.				

MANURE—

5.56 p.c.	6.75 p.c.	6.16 p.c.	7.49 p.c.	6.09 p.c.	7.40 p.c.
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Finally, a sample of pure ammonium sulphate was taken, which should contain, theoretically, 21.21 per cent. nitrogen, and on distilling the ammonia out of a known quantity I obtained 21.25 per cent. nitrogen. On treating another portion by the "Stock Method" I found 21.05 per cent. nitrogen. This shows that my standard solutions used in the analyses were practically correct.

On looking over the last six substances given above, one will observe that the higher the percentage of nitrogen the greater is the difference between the "Stock" figure and the Kjeldahl figure. However, the loss is not proportionate to the amount of nitrogen present, and, as will be seen from the following table, the percentage loss of nitrogen is by no means the same. Thus, in

The Linseed Cake the loss is 10.28 per cent of the total nitrogen present.

Hoofs and Horns	"	13.15	"	"	"
Fish Guano (1)	"	17.28	"	"	"
" (2)	"	10.63	"	"	"
Dried Blood	"	16.84	"	"	"
Manure	"	9.30	"	"	"

The percentage of nitrogen found by the Kjeldahl process is taken as being the true percentage of nitrogen in the substances examined. There are several possible explanations of the deficiency, and I will enumerate a few of these.

(i.) The nitrogen in the presence of so much oxidizing agent may be oxidized to nitric acid straight away, and so be driven off.

(ii.) The ammonium sulphate formed may be further oxidized into nitrogen itself, or into some volatile compound of nitrogen.

(iii.) There may exist two different nitrogenous components in the above substances, one of which yields up its nitrogen, forming ammonium sulphate, while the other nitrogen is driven off by the strongly oxidizing mixture.

(iv.) The loss may result from some defect in the manipulation of the analyses, and this is, to some extent, borne out by the analyses I have given above. In the first experiments made it will be seen that the figures obtained

by both methods agreed fairly well with each other. It so happens that in these early analyses the manganese dioxide was added slowly, a little at a time, until I found out how much was required to quickly complete the oxidation and produce the green colour, which Mr. Stock says is an indication that the reaction is complete.

As soon as the requisite quantity was ascertained, it was added bodily to the substances, of which I afterwards give the figures. It is conceivable that in this case the large amount of oxygen present at one time was too much for the nitrogen, and that it is driven off, while in my former experiments the gradual addition of the manganese dioxide may only have produced sufficient oxygen to oxidize the sulphurous acid formed as the heating went on. When the substance was decomposed the green colour appeared, and no more dioxide was added. This part of the process requires further investigation, and I intend to do some more work on it.

I presume that a mixture of sulphuric acid and manganese dioxide acts on nitrogenous organic substances in much the same way as a mixture of sulphuric acid and potassium permanganate. It is known that the addition of potassium permanganate to a "Kjeldahl," even when all the organic matter is decomposed and the solution is colourless, may cause a considerable loss of ammonia.

In my experiments it always takes about ten minutes to a quarter of an hour to oxidize the substance. Mr. Stock says that he can carry out the operation in three to five minutes. Probably the difference in time required is due to the purity or impurity of the manganese dioxide used. Mine contains 40.86 per cent. of the dioxide. It is ordinary commercial powdered dioxide.

From the above experiments it is evident that the method requires a great deal more examination, and the cause of the loss of nitrogen discovering, together with, if possible, a preventative against the said loss, before the process can be used by analysts as a reliable one for the estimation of nitrogen in common organic substances.

DISCUSSION.

Mr. F. H. Perry Coste remarked, with regard to the results obtained by Mr. Skertchly, that in view of the very good correspondence between the figures in several instances, and also of the results on pure salts recently communicated by Mr. Stock himself, he did not attach much importance to the low nitrogen result with the ammonium sulphate; he had very little doubt that that was due to some oversight in working, and that Mr. Skertchly on repeating the experiments would obtain the full nitrogen.

The differences in the case of such samples as the *Hoofs and Horns* were, however, very important, for these might be taken as criteria; and any method that would yield the full nitrogen with such materials as these might safely be accepted as reliable for all ordinary work. Of course the differences were so great as to make it clear that the

Stock method was useless as a general analytical process at present ; but no one who had had personal experience in working out the Kjeldahl process would be hasty in finally condemning this new process on such grounds. It required long experimenting to bring the Kjeldahl process into thoroughly reliable working order, and he well remembered that for many weeks results were obtained regularly too low, very much as with the Stock method in the present case. As to the cause of the error here, having regard to the concordance between Mr. Skertchly's duplicates, he did not think it likely that the low nitrogen was due to any error in working ; the results seemed to him too constant for that. Two sources of error were possible. The whole of the nitrogen might be converted into ammonia, and then some of it oxidised into a nitrogen oxide by the continued action of the manganese oxide, just as he had found that a heavy loss of nitrogen might occur in the Kjeldahl process if, at the end of the digestion, permanganate were added and the digestion renewed. This was a *time reaction*, for instance, he (Mr. Coste) had proved in Dr. Dyer's laboratory several years ago that if pure ammonium sulphate sulphuric acid and mercury were boiled with potassium permanganate for increasing periods of time, increased losses of nitrogen took place. Now, if Mr. Skertchly would treat these samples by the Stock method for various times (say 5 to 10 or 15 minutes) then, if he found increasing losses of nitrogen, that would point to a similar danger. If, however, in such experiments the nitrogen remained constant though still too low, that would strongly point to the second possible cause of error being present, viz., that the nitrogen in such samples exists in at least two different forms, and that the Stock process fails to convert the whole. Considering the nature of these samples, that explanation had frequently suggested itself to Dr. Dyer and himself ; and this would account both for the agreement between Mr. Skertchly's duplicate "Stocks," though both so low, and also for the correct results obtained from other samples of a similar character. He hoped that Mr. Skertchly would continue these experiments, which were of great interest and value.

Dr. Bernard Dyer said that he himself had not yet found time to make any experiments with Mr. Stock's process. He was very anxious to get some personal experience of the process, and had been very pleased to give Mr. Skertchly those samples, so that by comparing results, he was enabled to get some indirect personal experience of what results the Stock process gave on materials of which he knew the composition.

The President wished to ask Mr. Skertchly whether he followed exactly the plan proposed by Mr. Stock, or in what way he altered it? Did he use the same quantities which Mr. Stock proposed, and did Mr. Stock lay down any rules as to the adding of manganese dioxide?

Mr. Coste assumed that in all these cases the distillations after the digestion in the Stock and Kjeldahl processes were carried out under equal conditions as to time and everything else.

Dr. Dyer, in reply to the question of a member, said that he had found no difficulty in obtaining acid which yielded practically no nitrogen. When a new bottle of acid was opened or a stock of caustic soda was made up, a complete blank experiment was made, going through the whole process, except that no nitrogenous substance was used, and the total allowance indicated for error and impurities from all sources came well within half a milligramme of nitrogen. There was no difficulty in getting sulphuric acid as pure as this.

Mr. Skertchly, in reply, said that as Mr. Stock had only used such small quantities, namely 0.5 to 1.0 gramme of the substances for analysis, he had thought it better to take somewhat larger amounts, up to 2 grammes. He first tried the process using the smaller quantity and the results thus obtained did not agree so well between themselves as when he used 2 grammes of the substance. Two grammes would give a better average sample than 0.5 gramme. With the larger amounts double the quantities of sulphuric acid and manganese dioxide were used. As to Mr. Coste's question, he would like to say that he gave one experiment with ammonium sulphate 10 minutes, and another three-quarters of an hour heating on the sand bath, and obtained the same results in both cases. With regard to the distillations, they were carried out under practically the same conditions.

He wished to thank Mr. Hehner for his kind assistance during the investigation.

The President said he was very glad to see that the Society had in Mr. Skertchly a new acquisition to those who read papers. It was highly desirable that young chemists, who became members, should attack matters requiring investigation, and give the Society the benefit of their experience.

Mr. Richmond read papers "On the action of some Enzymes on Milk-Sugar," and "The Estimation of Total Solids in Milk." With this the proceedings of the Society terminated.

NEUTRALITY.*

BY ALFRED H. ALLEN.

(Continued from page 192.)

I may say here that there appear to be good and bad kinds of methyl-orange in commerce, some giving very unsatisfactory results. I have elsewhere given the characters of a good article. In this connection I may mention that the colouring matter known as orange II. (helianthin being orange III.), or betanaphthol-orange, behaves in exactly the opposite manner to methyl-orange, becoming yellow in acid solutions and red in alkaline. Further, I have found it almost indifferent to ammonia. Unfortunately its reaction, even with caustic soda, is not sufficiently sharp to render it of practical value, or we should be in possession of a valuable indicator which would permit us to titrate caustic soda in presence of ammonia. Some valuable applications of such an indicator, if sufficiently delicate, at once suggest themselves.

* Abstract of a lecture delivered before the Chemists' Assistants' Association.

Dimethyl-amido-azobenzene itself, the colouring matter of which methyl-orange is the sodium sulphonate, has been recommended as an indicator by Fischer and Philipp, but R. T. Thomson considers it in no way superior to helianthin, the behaviour of which it in every way simulates. *Congo-red*, another indicator of the same class, is distinctly inferior to methyl-orange.

Mylius and Förster have suggested a method of titration in which iodeosin is employed. This colouring matter, though chemically related to phenolphthaleïn, as an indicator behaves like methyl-orange. That is to say, it is a tolerably strong acid itself and hence is not displaced from its compounds by very weak acids. Iodeosin presents no advantage when substituted for methyl-orange in ordinary titrations, but Mylius and Förster employ it in ethereal solution. Immediately there is the least excess of alkali the sodium salt is formed, and the colouring matter passes from the ethereal to the aqueous layer. With special care, and the use of water distilled in platinum, very minute traces of alkali can be determined in this way. (*cf.* THE ANALYST, xvi., p. 199.)

The explanation of the different behaviour of various indicators has received help from the thermo-chemical researches of Berthelot, who has pointed out that an acid which can be titrated accurately with methyl-orange is one the heat-formation of the solid potassium salt of which exceeds 10·2 calories. Phenolphthaleïn, on the other hand, enables us to titrate any acid the heat-formation of the potassium salt of which exceeds 6 to 7 calories. With Poirrier's soluble blue still feebler acids can be titrated, but the lower limit of its applicability has not been ascertained.

Mr. R. T. Thomson, of Glasgow, has investigated the behaviour of different indicators of neutrality in a remarkably complete and able manner, and his researches form in themselves a most valuable guide to the subject. I am indebted to Mr. Thomson's work for many of the facts respecting indicators mentioned in this paper. Mr. Thomson arranges the various indicators in three groups, to which Poirrier's soluble blue will form a fourth, thus :—

Methyl-Orange Group.	Litmus Group.	Phenolphthaleïn Group.	Poirrier's Soluble Blue.
Methyl-orange Cochineal Congo-red Lacmoid Iodeosin Dimethyl-amido-azobenzene	Litmus Rosolic acid Phenacetolin	Phenolphthaleïn Turmeric	Soluble Blue CLB.

In the following table, which, with the exception of the last column, is due to Mr. R. T. Thomson (*Jour. Soc. Chem. Ind.* vi., 198), the figures represent the number of atoms of hydrogen displaced by sodium or potassium in the form of caustic alkali, when

a compound is formed having a neutral reaction to the indicator in question. Thus, when methyl-orange is used in the titration of sulphurous acid, the neutral point is reached when alkali has been added in quantity sufficient to form the compound NaHSO_3 ; but when phenolphthaleïn is used the point of neutrality corresponds to the salt Na_2SO_3 . By a combined use of the two indicators some valuable volumetric determinations can be affected.

Acids.			Methyl Orange.	Phenolphthaleïn.		Litmus.		Poirrier's Soluble Blue CLB.
Name.		Formula.	Cold.	Cold.	Boiling.	Cold.	Boiling.	Cold.
Sulphuric ...	...	H_2SO_4	2	2	2	2	2	2
Hydrochloric ...	...	HCl	1	1	1	1	1	1
Nitric ...	...	HNO_3	1	1	1	1	1	1
Thiosulphuric ...	...	$\text{H}_2\text{S}_2\text{O}_3$	2	2	2	2	2	?
Carbonic ...	...	H_2CO_3	0	{ 1 dilute }	0	—	0	2
Sulphurous ...	...	H_2SO_3	1		—	—	—	2
Sulphydric ...	...	H_2S	0	{ 1 dilute }	0	—	0	?
Phosphoric ...	...	H_3PO_4	1		—	—	—	3
Arsenic ...	...	H_3AsO_4	1	2	—	—	—	3
Arsenious ...	...	H_3AsO_3	0	—	—	0	0	3
Nitrous ...	...	HNO_2	{ indicator destroyed }	1	—	1	0	?
Silicic ...	...	H_4SiO_4		—	—	0	0	?
Boric ...	...	H_3BO_3	0	—	—	—	—	1
Chromic ...	...	H_2CrO_4	1	2	2	—	—	?
Oxalic ...	...	$\text{H}_2\text{C}_2\text{O}_4$	—	2	2	2	2	2
Acetic ...	...	$\text{HC}_2\text{H}_3\text{O}_2$	—	1	—	{ 1 nearly }	—	1
Butyric ...	...	$\text{HC}_4\text{H}_7\text{O}_2$	—	1	—		—	1
Succinic ...	...	$\text{H}_2\text{C}_4\text{H}_4\text{O}_4$	—	2	—	{ 2 nearly }	—	1
Lactic ...	...	$\text{HC}_3\text{H}_5\text{O}_3$	—	1	—		1	1
Tartaric ...	...	$\text{H}_2\text{C}_4\text{H}_4\text{O}_6$	—	2	—	2	—	2
Citric ...	...	$\text{H}_3\text{C}_6\text{H}_5\text{O}_7$	—	3	—	—	—	3

The behaviour of the alkaloids and organic bases with indicators has been very imperfectly studied. In the text-books it is frequently stated that such and such an alkaloid is distinctly alkaline (presumably to litmus), but it is only rarely and of recent years that chemists appear to have attempted to estimate alkaloids by titration with standard acid. Where this is desired, phenolphthaleïn is quite inapplicable, as already stated. Litmus answers in some cases, but by no means invariably, while with methyl-orange, in nearly all the cases hitherto tried, an accurate determination and a sharp end-reaction are obtainable.

In titrating an alkaloid with methyl-orange, it is rarely convenient to employ an aqueous solution of the base. A solution in proof spirit can be employed, but the indicator is much less sensitive under such conditions. I have found it preferable, especially when an alkaloid is much coloured, as is frequently the case in assaying bases directly extracted from their sources, to dissolve the alkaloid in a little ether, chloroform, amyl alcohol, or other suitable immiscible solvent. The solution is placed in a small stoppered cylinder, together with a few centimetres of water, coloured with a drop of methyl-orange solution. On then gradually dropping in the standard acid and agitating thoroughly after each addition, it is easy to observe the end of the reaction, as the colouring matter remains in the immiscible layer and presents a marked contrast to the red colour of the aqueous liquid. By using ether as a solvent for the alkaloid and titrating with $\frac{N}{50}$ hydrochloric acid, I have obtained very satisfactory determinations of aconitine and its allies, even when working on as little as 0.030 gramme. This means the titration of the alkaloids from as little as three or four ounces of the tincture, or less than half-an-ounce of the aconite root.

In the following table I have compiled all the available information on the subject of the titration of alkaloids. The behaviour of numerous other alkaloids can be guessed at, but I have preferred to omit speculative statements. In the column headed 'methyl-orange,' accurate titrations can be made where the word *alkaline* is printed in italics. Where blanks are left the exact behaviour of the alkaloid is unknown.

It is evident that much remains to be done in this direction, and if some of the members of the Society will take the trouble to fill some of the gaps they will be doing a good work, and one which will be generally appreciated.

Substance.	Formula.	Methyl Orange.	Phenolphthalein.	Litmus.
Methylamine	CH_5N	<i>Alkaline</i>	—	Alkaline
Trimethylamine	$\text{C}_3\text{H}_9\text{N}$	<i>Alkaline</i>	—	Alkaline
Aniline	$\text{C}_6\text{H}_7\text{N}$	Alkaline	Neutral	Neutral
Pyridine	$\text{C}_5\text{H}_5\text{N}$	<i>Alkaline</i>	Neutral	Alkaline
Quinoline	$\text{C}_9\text{H}_7\text{N}$	<i>Alkaline</i>	—	—
Antipyrine	$\text{C}_{11}\text{H}_{12}\text{N}_2\text{O}$	<i>Alkaline</i>	Neutral	Neutral
Conine	$\text{C}_8\text{H}_{17}\text{N}$	<i>Alkaline</i>	Alkaline	Alkaline
Nicotine	$\text{C}_{10}\text{H}_{14}\text{N}_2$	<i>Alkaline</i>	Alkaline	Alkaline
Aconitine	$\text{C}_{33}\text{H}_{45}\text{NO}_2$	<i>Alkaline</i>	Neutral	Alkaline
Atropine	$\text{C}_{17}\text{H}_{23}\text{NO}_3$	<i>Alkaline</i>	Alkaline	Alkaline
Cocaine	$\text{C}_{17}\text{H}_{21}\text{NO}_4$	<i>Alkaline</i>	Neutral	Alkaline
Morphine	$\text{C}_{17}\text{H}_{19}\text{NO}_3$	<i>Alkaline</i>	Faintly acid	Alkaline
Codeine	$\text{C}_{18}\text{H}_{21}\text{NO}_3$	<i>Alkaline</i>	Alkaline	Alkaline
Strychnine	$\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_2$	<i>Alkaline</i>	Neutral	Alkaline
Brucine	$\text{C}_{33}\text{H}_{26}\text{N}_4\text{O}_4$	<i>Alkaline</i>	Neutral	Alkaline
Cinchona bases	—	<i>Alkaline</i>	Neutral	Alkaline
Caffeine	$\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$	Alkaline	Neutral	Neutral
Urea	$\text{CH}_4\text{N}_2\text{O}$	Neutral	Neutral	Neutral

As an illustration of the application of the foregoing facts, we may take the case of a mixture of cinchona alkaloids. In the analysis of these the cinchonidine is usually precipitated from a neutral solution by means of Rochelle salt; the precipitate washed with cold water (thereby causing an uncertain loss), dried and weighed. Now, if, instead, the precipitate be washed once with a saturated solution of the precipitant (which has very little solvent action) and the filter containing the precipitate of cinchonidine tartrate and the adherent Rochelle salt be immersed in boiling water, the alkaloid can be determined in a few minutes by adding a drop of phenolphthaleïn solution and titrating with $\frac{N}{20}$ caustic alkali. As Rochelle salt is perfectly neutral to phenolphthaleïn, and as tartrate of cinchonidine (or of quinine) acts just like an equivalent amount of free tartaric acid, the weight of alkaloid can be readily calculated from the measure of standard alkali used. Each 1 c.c. of $\frac{N}{20}$ NaHO neutralised represents 0.0147 gramme of cinchonidine or (other alkaloid) precipitated as tartrate.

An exactly similar method is applicable to the treatment of the precipitate of quinidine hydriodide. This should be washed with a little neutral solution of potassium iodide instead of with water, and then immersed with the filter in boiling water. On titrating with $\frac{N}{20}$ caustic alkali and phenolphthaleïn, each 1 c.c. of the standard solution represents 0.0162 gramme of quinidine precipitated as hydriodide. Of course this does not dispense with the necessity of making a correction for the amount of quinidine lost in the mother-liquor and washings.

Hübl's Iodine-Absorption Method. (*Helfenberger Annalen*, 1891, through *Chem. Zeit.* Compare THE ANALYST, xvii. 199.)—Investigations made in the chemical works of E. Dieterich, at Helfenberg, upon the Hübl method have led to the following conclusions:—

(1.) When the iodine solution is allowed to act for twenty-four hours or longer, and the absorption of the oil reckoned from comparison with a blank experiment made at the time of adding the iodine to the oil, the results obtained are too high, as the Hübl solution itself loses strength on keeping. The value obtained is higher the higher the temperature, the more recently the Hübl solution has been made up, the greater the excess of iodine, and the longer the time allowed for the completion of the reaction.

(2.) Results that are demonstrably too low, seeing that they may even be lower at twenty-four than at two hours, are obtained by taking the strength of the iodine solution as determined by a blank titrated at the end of the period of absorption, for the reason detailed in the foregoing abstract.

(3.) When a correction is made for the loss of strength of the excess only of the iodine solution as reckoned from the loss of strength of the blank titration during the period of absorption, the conditions recorded above as affecting results cease to exercise

any appreciably disturbing influence. (Contrast Holde's view—in preceding abstract—which is only tenable with the proviso that the large excess of iodine prescribed by him be used.)

(4.) Olive oil, tallow, oleic acid and lard give accurate iodine absorptions after two hours. Linseed oil, balsams, and resins, on the contrary, need longer exposure; (presumably, from the context—though it is not expressly stated—twenty four hours).

Holde's contention that a large excess of iodine is necessary, is found by Dieterich to be true chiefly for drying oils. He considers that there should be an excess sufficient, in the case of drying oils, to use up 20-30 c.c. of decinormal thiosulphate, while an excess corresponding to 10-20 c.c. suffice for non-drying oils. The importance ascribed by Holde to the age of the Hübl solution is only legitimate as far as it implies that the solution should be rich in available iodine; otherwise more of it must be used.

The combined opinion of Fahrion, Holde (see preceding abstract), and Dieterich is that the solutions of mercuric chloride and iodine should be kept separate until one or two days before use, as the waste due to spontaneous weakening is less, but that solutions mixed *immediately* before use should not be employed, as the change in strength is greatest directly after mixing, and the alteration is too rapid to allow of accuracy.

B. B.

REVIEW.

THE PRINCIPAL STARCHES USED AS FOOD. W. GRIFFITHS. (Baily & Son, Cirencester, Price 5/-.)

This handy little book contains a short and concise description of some twenty-four varieties of the principal starches usually met with, each being illustrated by a photograph. Though excellent illustrations of these objects are to be found in works on Botany, Food Analysis, &c., in the form of copper-plate engravings, lithographs or wood cuts, this is the first time, to our knowledge, that they have been portrayed by photography and collected in book-form. The best method of identifying an unknown starch is the somewhat tedious one of comparing it with actual samples of other starches under the microscope; the next best is undoubtedly to use for comparison a series of well-executed photographic representations of such samples. This latter function the book fulfils admirably; the illustrations are beautifully clear and distinct, the characteristics of each individual starch being prominently brought out. Specially interesting is the photograph of the not-generally-known starch from the fruit of the potato, which the author characterises as "the most beautiful of all starches." It somewhat resembles that of the tuber, but is much larger.

The book cannot fail to be of value to analysts, who are so frequently called upon to identify starches used for the purpose of adulteration.